NEW HAMPSHIRE
DEPARTMENT OF
Environmental
Services

Guidelines for Selection of Natural Attenuation for Groundwater Restoration

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STATE OF NEW HAMPSHIRE
DEPARTMENT OF ENVIRONMENTAL SERVICES
WASTE MANAGEMENT DIVISION

GUIDELINES FOR SELECTION OF NATURAL ATTENUATION FOR GROUNDWATER RESTORATION

1. PURPOSE AND SCOPE

    1. This policy provides guidance for the selection of natural attenuation as a remedial measure to restore groundwater contaminated with volatile organic compounds (VOCs) to Env-Ws 1403 Ambient Groundwater Quality Standards (AGQS). VOCs include both chlorinated and non-chlorinated compounds. This policy does not apply to sites contaminated with inorganic compounds, or to contamination in the unsaturated zone.
    2. DES recognizes that remediation by natural attenuation (RNA) has been a remedial component at many existing sites, and expects frequent use of RNA to continue. For these sites, this policy represents the initial effort by the Department of Environmental Services (DES) to establish guidelines to evaluate and monitor the effectiveness of RNA as a remedy to groundwater contamination.
    3. This policy defines the general conditions under which RNA may be considered as a remedial component for contaminated sites in New Hampshire. DES recognizes that subsurface conditions and remedial requirements vary substantially among sites. *Given this fact, DES also recognizes that this policy must accommodate the experience and judgement of the responsible party (RP) and their consultant. DES expects the RP and their consultant to carefully consider specific site conditions and recommend the level of work that is appropriate for the site.*
    4. This policy is intended solely as guidance and does not contain mandatory standards except where found in statutes, or where administrative rules are referenced.

2. REGULATORY BACKGROUND

    1. The New Hampshire Code of Administrative Rules Part Env-Wm 1403 (Groundwater Management and Groundwater Release Detection Permits) were developed in February 1999 under the statutory authority of RSA 147-F:18 and RSA 485-C:4. Key features of Env-Wm 1403 are to prevent groundwater contamination, protect public health and the environment, and remediate groundwater contamination. Env-Wm 1403.08 summarizes the requirements for remedial actions at contaminated sites and requires submission of a Remedial Action Plan (RAP) to the Department which includes a remedial alternatives analysis, and outlines the overall remedial strategy and specific remedial design components for a given site. Env-Wm 1403.09 summarizes the criteria used by DES in the evaluation of appropriateness, feasibility, and effectiveness of remedial methods. The RAP is a site-specific document, and is required to achieve the following hierarchy of objectives:

1. remove, treat or contain the source of the groundwater contamination to prevent the release of additional contaminant mass to groundwater;
2. delineate a Groundwater Management Zone (GMZ) which contains the estimated maximum extent of the contaminant, and implement administrative controls to ensure that untreated groundwater within the GMZ cannot be used for consumptive purposes;
3. restore groundwater quality to meet the Agroundwater quality criteria@ established under Env-Wm 1403.05.

2. Although these rules do not specifically address RNA, DES does allow implementation of RNA as a remedial component in certain cases, providing the relevant requirements of Env-Wm 1403 are met. Under favorable conditions, RNA may be selected as the preferred remedial approach to address groundwater contamination.

3. DEMONSTRATING EFFECTIVENESS OF NATURAL ATTENUATION

1. RNA in this policy is defined as the naturally-occurring processes in the environment that act, without human intervention, to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in groundwater. These processes include biodegradation, dispersion, sorption, volatilization, and/or biological or chemical stabilization or destruction.

2. DES encourages the use of monitored RNA for remediation of dissolved phase contaminated groundwater at sites where:

    1. it is demonstrated to be protective of human health and the environment and meets other requirements of Env-Wm 1403.09;
    2. it is demonstrated to present no additional risk to receptors;
    3. evidence of a stable or receding plume is provided;

4. biodegradation or other destructive processes are demonstrated to be occurring;
5. remedial goals will be achieved within a reasonable period of time (as defined in Section IX) including reduction of groundwater contaminant concentrations below AGQS.

3. It is the responsibility of the RP to demonstrate to the DES that RNA will meet the criteria listed above. DES may impose additional requirements on a site specific basis.

A. Hydrogeologic Data

1. DES will not approve site investigations (SI) or RAPs proposing RNA without adequate site-specific supporting data. These documents must demonstrate that RNA will be effective in achieving remedial goals within a reasonable period of time. In some cases, the amount of SI information required to support RNA will exceed that required for active remediation sites.

2. As required for any site investigation, care must be taken to adequately characterize hydrogeologic conditions including lithology, groundwater flow patterns, groundwater gradients, hydraulic conductivity and its variability, recharge mechanisms, background hydrogeochemistry, nature of groundwater fluctuations, the nature and extent of the contamination, effects of sorption and hydrodynamic dispersion, and relevant physiochemical and biological processes. This information is particularly important for RNA proposals because the natural hydrogeological conditions will be solely relied upon to provide management of the contaminant plume. Identification of vertical gradients is particularly important in cases where bedrock drinking water supply wells are near the site, or the site is located in an identified groundwater recharge area. The type, location, concentration and quantity of the contaminant source(s) need to be identified for all affected areas and media.

3. All contaminant migration pathways of concern in terms of air, water, land and human contact should be identified during the investigation.

4. Estimation of contaminant travel time is essential for the determination of plume status and the effectiveness of RNA. Large errors in groundwater seepage velocity and travel time estimates can result from errors in estimation of the saturated hydraulic conductivity. Care should be taken to determine saturated hydraulic conductivity as accurately as possible. DES encourages the use of slug tests to allow

more accurate estimation of hydraulic conductivity. Data analysis should be performed with traditional test methods (e.g., Hvorslev, 1951; Bouwer and Rice, 1976; Bouwer, 1989) or an equivalent, pre-approved method. Due to errors inherent in the tests and variability in subsurface conditions, the tests should be performed in multiple wells. Uncertainties resulting from these errors should be clearly stated.

5. Grain-size analyses are also an effective means to estimate saturated hydraulic conductivity for sands which do not contain appreciable amounts of fine silt and clay-size particles (Freeze and Cherry, 1979). These analyses may be conducted using sieve and hydrometer methods (ASTM D422-63). Empirical relationships may be used to estimate hydraulic conductivity from grain-size distribution curve characteristics. This approach has seen a recent renaissance in some of the stratified-drift aquifer evaluation studies performed by the USGS in New Hampshire (Moore, 1990; Stekl and Flanagan, 1992; Ayotte and Toppin, 1995; Moore and Medalie, 1995).

6. At large or more complex hydrogeological sites, and in cases where greater risk to receptors exist, the use of pumping tests should be considered to estimate hydraulic conductivity.

4. Evidence of Natural Attenuation

1. For all sites where RNA is proposed, a thorough evaluation of anticipated effectiveness must be provided. The effectiveness of RNA may be demonstrated using historical trends in contaminant, terminal electron receptor (TEA), and byproduct concentrations; and physical indicators (a.k.a. primary evidence), determination of rates of individual processes and quantitative evaluation of geochemical data (a.k.a. secondary evidence), or microbial evidence (a.k.a. third line of evidence) as further summarized below.

2. Primary Evidence

    1. Primary evidence should be evaluated for all sites. This should include evaluation of contaminant, TEA, and biodegradation byproduct concentrations trends over time in individual wells, and over distance near the plume centerline, unaffected by human intervention. Graphs illustrating these trends should be provided, as further described for periodic reporting in Section X. Actual plume extent should be compared with the

predicted extent assuming no biodegradation if the date of release can be reasonably estimated (McAllister and Chiang, 1994). Maps showing iso-concentration lines for the contaminants and their daughter products should also be provided.

2. Satisfactory primary evidence should clearly show concentration trends and plume status, provide a basis for estimation of remediation time, and demonstrate that destructive processes are occurring. The data must be evaluated with consideration of recharge history.

3. Secondary Evidence

   1. Secondary lines of evidence must include evaluation of the rate of RNA, using appropriate analytical or numerical modeling or graphical methods. Several techniques are summarized in ASTM (1997), Weidemeier et al (1995), Newell et al (1995), and Ollila (1996). A mass balance approach may be used if sufficient data is available (Chiang et al, 1989; McAllister and Chiang, 1994).

   2. Secondary evidence may be required in some cases including when:

      (1) inadequate historical concentration trend data is available (< 4 rounds of data over an adequate period of time);
      (2) there is no clear long-term decreasing trend in historical VOC concentration data, or the data is unreliable;
      (3) it is not possible to install a well and obtain groundwater samples at the GMZ boundary; and
      (4) a better understanding of the RNA processes is warranted.

   3. Secondary evidence may include modeling, as further described below.

4. Tertiary Evidence

   1. Biodegradability of petroleum compounds is well documented and bacterial availability is generally not a limiting factor (McAllister and Chang, 1994; Salanitro, 1993). Therefore, DES will generally not approve enumerations and microcosm studies at petroleum contaminated sites requesting reimbursement from the Petroleum Reimbursement Fund.

   2. Microcosm studies and enumerations may be considered if

the primary and secondary evidence is not satisfactory.

5. Modeling

1. Use of analytical or numerical models may facilitate understanding of the fate and transport mechanisms at a site, and allow prediction of the extent and life of the contaminant plume. Several proprietary and public domain models are available. Public domain models include BIOSCREEN (USEPA, 1997), BIOPLUME III (USEPA, 1998), and BIOCHLOR. BIOSCREEN and BIOCHLOR are 2-dimensional analytical screening level models; BIOPLUME III is a 2-dimensional numerical model. BIOSCREEN and BIOPLUME III are available at no cost from the US EPA Kerr Laboratory Web Page. The beta version of BIOCHLOR is available at no cost from the Groundwater Services, Inc. Web site. DES encourages use of proprietary or public domain models for sites where their use is appropriate.
2. Suitability of the model assumptions should always be evaluated relative to site hydrogeological conditions to ensure that they do not render the model inappropriate for use. Refer to Alvarez (1996) for an case study describing several effects of use of an inappropriate model. Caution must be used in the application of simple models to hydrogeologically complex sites. In some cases, the cost of site investigations needed to support numerical modeling will be prohibitive.
3. Models must be calibrated for the individual site. The value of a decay rate, if used, should be normalized to a conservative tracer (such as chloride, trimethylbenzene), or calculated using the method of Buscheck and Alcantar (Buscheck and Alcantar, 1995). For petroleum contaminated sites, the selected model should use TEA and byproduct concentrations to calculate losses due to biodegradation.
4. When there is a high degree of uncertainty regarding the magnitude of input parameters used in a model, the value of the parameters should be selected to err on the conservative side, i.e. tend to result in greater concentrations flowing at greater velocities. Sensitivity analysis should be performed by varying parameters used in the model to identify key input parameters having the greatest effect on predictions, and to quantify the uncertainty in the calibrated model. The results of sensitivity analysis should be presented in the report submitted to DES.
5. Published values may be used for selected input parameters

(K_{oc} and effective porosity, for example) if the model is relatively insensitive to variation of the particular value over a reasonable range, or if professional experience indicates that the published value is representative of conditions at the site. In such cases, justification should be provided.

6. Primary lines of evidence and simple analytical models should be relied upon whenever they are appropriate.

4. COMBINATION WITH OTHER REMEDIES

1. RNA will not be approved as the *sole* remedial strategy for contaminated groundwater at sites if separate phase product or another contaminant source continues to supply contaminant mass to the groundwater. In such cases, an approved source control measure must also be implemented unless:

   1. it can be demonstrated that the source will be short-lived and will not result in further plume expansion; or
   2. it can be demonstrated that it is infeasible to remove the source and the plume is not expanding.

2. RNA may be implemented in conjunction with other remedies as appropriate. A typical example is use of RNA for remediation of a groundwater plume, with active free product recovery or excavation in the source area. Another example is use of groundwater pump-and-treat in a highly contaminated portion of the plume and RNA in downgradient areas.

5. CONTINGENCY PLANS

1. Proposals for RNA must include a contingency remedial method that could be implemented if RNA does not achieve remedial goals. The contingency method should be flexible and allow modifications as information about a site is accumulated and the conceptual model is refined.

2. Criteria for implementation of the contingency plan include:

   1. evaluation of the plume status indicates it is expanding vertically or horizontally;
   2. no overall decreasing trend in contaminant concentrations is evident, or the rate of contaminant concentration decrease does not achieve performance standards;
   3. TEA and degradation byproduct concentrations do not indicate biodegradation or other destructive processes are occurring; and
   4. a change in local land or groundwater use occurs which affects the RNA process or increases receptor risk.

6. MONITORING WELLS

1. A sufficient number of monitoring wells should be installed to:

   1. measure groundwater flow direction(s) and horizontal and vertical gradients;
   2. identify trends in contaminant TEA and byproduct concentrations within the plume, source areas, and upgradient;
   3. monitor plume status (expanding, stable, receding);
   4. identify any receptors at risk;
   5. identify possible toxic biodegradation byproducts;
   6. detect new releases; and
   7. monitor progress towards achieving remedial objectives.

2. Install a *minimum* of one upgradient well outside the plume boundary to detect changes in background water quality and allow evaluation of availability of TEA's. *At least two* monitoring wells should be located within the plume to provide data on trends in contaminant and TEA concentrations over time and distance. One of these wells should be located near the source area. To detect further migration of the plume, locate *at least one* down-gradient sentinel well outside of the plume limits. This well should be located upgradient of potential receptors.

3. The number and location of down-gradient wells should depend on the distance to potential downgradient receptors, seepage velocity, flow directions, plume magnitude, lithology, hydraulic controls, vertical flow, and other factors. Additional wells should be installed as required to identify the lateral limits of the plume and identify or monitor any vertical plume migration. If possible, the upgradient, source area, and downgradient wells should be located along a flowpath near the plume center.

4. Well construction details, and the dates and methods of installation and development should be provided.

5. Measured contaminant, TEA and byproduct indicator concentrations may be misrepresented if wellscreens penetrate zones where a significant vertical contaminant concentration profile exists (Chiang et al., 1992; Robbins, 1989). This may affect evaluation of the existing plume extent and status, assimilative capacity, and predicted extent of the plume. Subsurface lithology and location of the contaminant plume should be carefully considered in the selection of wellscreen intervals. Short wellscreens and nested wells, or discrete sampling methods, should be used where significant variability

is anticipated.

7. GENERAL GUIDELINES FOR NATURAL ATTENUATION PROPOSALS

1. At many petroleum contaminated sites, DES expects that RNA will be proposed as an effective remedial option within the SI phase. If the hydrogeochemical data establish that RNA will prove effective in a reasonable period of time and there is no additional risk to receptors, the site investigation should recommend RNA as the preferred remedial option.

2. The decision to approve RNA without a remedial action plan will be made on a case by case basis. The RP and their consultant should discuss this possibility with the DES project manager before and during the site investigation phase so that appropriate supporting information is obtained.

3. For non-petroleum sites, RP=s and/or their consultants are encouraged to confer with the Hazardous Waste Remediation Bureau (HWRB) during the SI phase to develop a site-specific list of criteria and supporting information that DES would require to demonstrate RNA and consider its use as a remedial component.

4. All RAPs for petroleum contaminated sites must include an evaluation of RNA as a remedial alternative. The minimum data requirements described above for site investigations also apply to remedial action plans. If still valid, data collected during the site investigation phase should be used to satisfy this requirement.

5. A RAP or SI which proposes RNA must include a monitoring plan. The monitoring plan for RNA should include anticipated sampling frequency, location, type of measurements and samples, and a list of analytical parameters. The frequency of monitoring should take into consideration the site hydrogeology and the ability to gather representative information on contaminant trends and plume status. Monitoring must be conducted at a frequency appropriate to detect significant changes in the contaminant plume, specifically changes in contaminant concentrations over time and distance. The proposal for RNA should also include performance criteria.

8. SAMPLING AND ANALYSIS

1. To support any proposal for RNA, DES generally requires a minimum of four sampling rounds representative of hydrogeological conditions over an adequate period of time. Each sampling round should include all applicable parameters listed in Table 1. Note that an initial round, and a

confirmatory round completed several weeks later does not qualify as two rounds.

2. RNA may be proposed in an SI report, possibly making preparation of a remedial action plan unnecessary. The SI report should provide an evaluation of the anticipated effectiveness of RNA, and a discussion of the uncertainty of the evidence provided. If inadequate supporting data is provided (e.g., only two rounds of monitoring data) preparation of a supplemental site investigation report may be required.

3. Analyses from subsequent rounds may be limited to those contaminants previously detected and other relevant parameters, including TEAs and byproducts identified in the first round and required for the evaluation of remedial progress. *The parameter list and frequency of analysis for RNA parameters should be discussed with the DES project manager. It is generally not necessary to perform analyses for RNA parameters with each sampling round.*

4. Laboratory and field analysis techniques are available for many of these parameters. DES requires field determination of dissolved oxygen, pH and oxidation reduction potential (ORP). Field determination for other parameters is acceptable in cases where reliable field test methods are available. Field test kits are available from several vendors. Use of down-hole probes should be considered for some parameters. Samples that are taken to a lab must be properly prepared and handled to ensure accuracy of data. Samples intended for dissolved metals analyses must be filtered and preserved in the field.

5. To obtain accurate results, wells should be purged slowly to avoid aeration of the groundwater. This is particularly important for ferrous iron, dissolved oxygen, ORP and methane.

6. A summary of sampling and test methods, their associated advantages and disadvantages, and application recommendations are included in the manual by the American Petroleum Institute (API, 1997b). The manual indicates that the use of a peristaltic pump to obtain samples has been reported to result in the loss of 40% of dissolved methane. Ferric and ferrous iron may interfere with measurement of dissolved oxygen using the iodometric method (American Public Health Association, 1995). The advantages and disadvantages of various sampling and test methods should be carefully considered. Justification of the methods used should be provided. Methods and equipment that yield suspect data may not provide convincing support for RNA proposals.

7. Analyses for total organic carbon should also be performed if needed to quantify the amount of carbon available for reductive dechlorination at chlorinated solvent contaminated sites; or to determine the concentration of TEA scavenging non-target organic contaminants.

9. REMEDIATION TIME

1. Remediation time is the predicted time needed to restore groundwater quality to achieve remedial goals. DES requires that the remediation time be Areasonable@, based on site specific criteria including the proximity and presence of receptors, aquifer use, contaminant characteristics, geologic and hydrogeologic conditions and the use of institutional controls (e.g. USEPA, 1997). In some cases, RNA alone may not restore groundwater contamination within a reasonable period of time without implementation of supplemental remedies.

2. DES uses 10 years as a default value for an acceptable, reasonable remediation time at sites where RNA is proposed. This time period may be increased or decreased based on information presented in the SI or RAP, subject to DES approval. The proposal must provide a rational argument for modification of the default time and address the following:

   1. resource value of the affected groundwater, considering present and anticipated future uses;
   2. time frame in which portions of the aquifer might be needed for a future water supply, considering the possibility of alternate supplies;
   3. uncertainties regarding contaminant mass, reactions, and fate and transport assumptions;
   4. reliability of monitoring and institutional controls (such as the GMZ and deed recordation);
   5. comments from the public regarding the remediation time; and
   6. ability of the RP to fund monitoring and evaluation over the remediation time period (petroleum reimbursement fund eligibility provides adequate proof of ability to pay).

10. PERIODIC REPORTING

1. Reports submitted to DES as required by the provisions of a Groundwater Management Permit should be used to convey results of RNA monitoring. Unless DES directs the responsible party otherwise, this report shall be submitted annually.

2. Each annual report should provide a tabular summary of contaminant, TEA and byproduct concentrations, and water level elevations. The summary should include data obtained in previous sampling rounds. Water table maps and contaminant concentration maps should be presented showing flowlines and

plume geometry history. Contaminant, TEA and byproduct, and other relevant physiochemical data should also be presented in X-Y or 3-dimensional graphs, where the *X-axes represent distance along the plume centerline*. Additional graphs should also be included showing temporal trends in VOC concentration, with a reference line showing the performance standards established in the Groundwater Management Permit.

3. The report must include an evaluation of plume status, an evaluation of natural attenuation pathways, and an assessment of the effectiveness of RNA in meeting the performance goals. It should also provide any recommendations for modification of the monitoring plan, implementing continency plans, or other appropriate work.

4. If a model was used to aid in the current evaluation of the progress of RNA, current input parameters and results should be submitted.

5. Monitoring must continue until remedial objectives are achieved consistent with the requirements of the site=s Groundwater Management Permit.

6. Refer to Borden et. al (1995) and Wiedemeier (1995) for examples of a thorough natural attenuation evaluations.

11. SITE CLOSURE

1. To obtain a Certificate of No Further Action (site closure), historical monitoring data must clearly demonstrate that:

   1. there is no active source of groundwater contamination on the site; and
   2. there has been an overall decreasing trend in VOC concentrations in groundwater, with groundwater quality presently meeting Ambient Groundwater Quality Standards for at least two consecutive sampling rounds.

2. Sites at which a contained source, or potential source, remains in place are not eligible for closure. These will require some level of on-going, confirmatory monitoring under a Groundwater Management Permit.

Table 1
Analytical Parameters for Natural Attenuation Sites

Parameter	Purpose
Dissolved Oxygen (DO)	Identify reducing zones, estimate assimilative capacity. Dissolved oxygen is an electron acceptor, assimilative capacity must be based on delta DO, compared to upgradient concentration.
Nitrate (NO_3^-)	Identify reducing zones, estimate assimilative capacity. Nitrate is an electron acceptor, assimilative capacity must be based on delta NO_3 , compared to upgradient concentration.
Sulfate (SO_4^{2-})	Identify reducing zones, estimate assimilative capacity. Sulfate is an electron acceptor, assimilative capacity must be based on delta SO_4 , compared to upgradient concentration.
Methane (CH_4)	Identify reducing zones, estimate assimilative capacity. Methane is a byproduct of the biodegradation reaction. Assimilative capacity is based on the measured CH_4 concentration
Ferrous Iron (Fe^{2+})	Identify reducing zones, estimate assimilative capacity. Ferrous iron is a byproduct of the biodegradation reaction. Assimilative capacity is based on the measured Fe^{2+} concentration
Soluble Manganese (Mn^{2+})	Identify reducing zones, estimate assimilative capacity. Soluble manganese is byproduct of the biodegradation reaction. Assimilative capacity is based on the measured Mn^{2+} concentration
Chloride (in some cases)	Indication of biological dechlorination; may be used as a conservative tracer
Oxidation Reduction Potential (ORP)	Identify reducing and oxidizing zones. Validate DO measurements.
Total Organic Carbon (in some cases)	Quantify mass of carbon source for reductive dechlorination at chlorinated solvent sites; quantify total contaminant mass to adjust TEA concentrations for Ascavenging@ organics
pH	Identify zones where biodegradation is occurring. Biodegradation releases CO_2, reducing pH. Reduction in pH below background levels may indicated zones of biodegradation. Affects viability of degrading contaminant organisms.
ethanes, ethenes	Identify breakdown products of chlorinated solvents
VOCs, daughter products	Provide evidence of plume status and decreasing trend. Monitor production of toxic by-products

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The following documents contain useful information regarding the theory and practice of RNA. Several of these documents are referenced in this policy.

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